*Bulletin of Electrochemistry* 15 (1) January 1999, pp 18-22

0256-1654/99/$ 3-50


# PREPARATION AND CHARACTERIZATION OF ANODES AND CATHODES FOR MOLTEN CARBONATE FUEL CELLS

G PRABHU, C SOLAIYAN, S DHEENADAYALAN, I ARULRAJ
S MUZHUMATHI, R CHANDRASEKARAN AND R PATTABIRAMAN

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

[Received: 2 September 1998 Accepted: 13 November 1998]

**Nickel powder(INCO 255) was used to prepare the electrodes. The anode was a porous nickel plate. Pure Ni and (Ni + 10% Cr) anodes were also fabricated. Several batches of electrodes were prepared by different techniques like loose power sintering (LPS), slurry casting (SC), tape casting (TC) etc. These electrodes were sintered in flowing hydrogen atmosphere at 1073 K (except in the case of Cr containing electrodes where it was 1173 K) for one hour. The cathode was mostly composed of porous nickel oxide plate. The nickel electrodes were usually got lithiated and oxidized inside the cell. The prelithiated nickel oxide powders were prepared by solid state reaction of nickel and $Li_2CO_3$ and characterized by XRD and cast in the form of tapes using a doctor blade assembly.**

**Keywords: Cathodes and anodes, molten carbonate fuel cells.**

## INTRODUCTION

The molten carbonate fuel cell(MCFC) represents an efficient device for the conversion of chemical energy into electrical energy[1,2]. The attractive feature of MCFC is that a wide variety of fuels such as hydrogen, hydrocarbons, carbon monoxide and their mixtures (gasified coal or reformed gas) can be used. Fig. 1 shows the state of art materials for the electrodes and electrolyte structures. A typical fuel cell assembly consists of a porous nickel anode containing chromium to provide strength and sintering resistance (fuel electrode) and a porous lithium doped nickel oxide cathode (oxidant electrode) separated by the molten alkali carbonate electrolyte (62 mol% $Li_2CO_3$ and 38 mol% $K_2CO_3$) contained within a porous ceramic lithium aluminate matrix.

The cell is operated at 923 K, hydrogen is oxidized at the anode and oxygen in reduced at the cathode as per the following equations.

**Anode**

$$H_2 + CO_3^{2-} = H_2O + CO_2 + 2e \qquad (1)$$

$$CO + CO_3^{2-} = 2CO_2 + 2e \qquad (2)$$

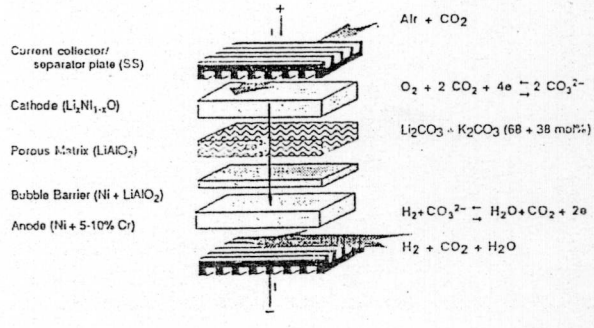


*Fig. 1: Schematic representation of the "state-of-art" molten carbonate fuel cell (Ref 1)*

athode

$$\frac{1}{2}O_2 + CO_2 + 2e = CO_3^{2-} \quad (3)$$

he fuel gas is a humidified mixture of $H_2$ + CO and the xidant is a mixture of $O_2$ + $CO_2$ which contain water apour.

he electrode materials must meet the following general equirements

- high electronic conductivity
- high electocatalytic activity
- thermodynamic stability
- chemical inertness -- moderate cost
- interconnected porosity
- ease of fabrication
- corrosion resistance in molten carbonate

/arious materials have been evaluated for use as anodes 3-6] and cathodes [7-9]. Efficient fuel cell operation requires hat the electrodes must have sufficient electrolyte to naintain the electrode/electrolyte reactant gas interface iecessary for the electrochemical reaction to occur. This equires a careful control of overall porosity and pore size listribution within the electrode structure [10-12]. The state of art specifications and the different electrode materials tudied are given in Table I.

/arious additives have also been reported in literature to tabilize the electrode structure and enhance the electrocatalytic activity [13-29]. The function of the additives is to reduce the loss of porosity during sintering and develop creep resistant materials. The creep is referred o as the shrinkage in thickness and change of shape. The sintering resistance is increased by the additives which are usually metals, or oxides of metals.

In this paper the characteristics of the anodes and cathodes prepared from INCO Ni powder are described.

## EXPERIMENTAL

Three types of Ni powders INCO 255, 287 and 123 were used. The metal powders were treated in hydrogen atmosphere as reported elsewhere [30]. The resulting powder was sieved through sieves and powders below 400 mesh were used to prepare the electrodes.

Similarly chromium powder was also treated. Ni + 10 wt% Cr mixtures were also prepared in a ball mill.

Porous electrodes were prepared by cold compaction at 190 MPa and loose powder spreading in graphite moulds. They were sintered in hydrogen atmosphere at 1123 K. The sintering temperature for Ni-Cr powders was 1173 K. The details of the sintering conditions are reported recently [31].

The slurry casting and tape casting procedures were also adopted to prepare thin green tapes/sheets of nickel. The process involves preparation of a slurry of nickel powder in water (solvent) with polyvinyl alcohol(PVA) liquid as the binder and glycerol as the plasticizer. The slurry was mixed and cast over a glass plate using a doctor blade assembly. The entire process is described in the flow sheet (Fig. 2). The cast bodies were removed from the glass substrate after 12 h of curing and stored.

The thickness, shrinkage and density measurements were carried out. These green tapes were flexible in nature. They were sintered in hydrogen atmosphere in a programmable furnace controlled at a heating rate 1 K/min. The porosity values were determined by liquid absorption technique.

## RESULTS AND DISCUSSIONS

The powder characteristics of the nickel powders after hydrogen treatments are shown in Table II and compared

**TABLE I: Typical characteristics of MCFC electrodes**

| | Anode | Cathode |
|---|---|---|
| Material | Nickel | NiO(lithiated) (3-5wt% Li) |
| Stabiliser | Chromium | ---- |
| Reinforcement screen | Nickel | SS |
| Porosity (Vol%) | 50-70 | 70-80 |
| Mean pore dia (μm) | 3-6 | 7-15 |
| BET surface area ($m^2/g$) | 0.1-1.0 | 0.1-0.50 |
| Thickness (mm) | 0.5-1.5 | 0.5-0.75 |
| Other additives or alternate materials | Cu[5], Co[14] Zr[15], Mg[16] Al[17] $Al_2O_3$[18,19] $LiAlO_2$[20] Cu-Ni Alloy[21,22] Ni-Al Alloy[23] Ni-Cr[24] | Ag[28] Perovskites [17,29] $LiCoO_2$[37] $Li_2Mn_3O_4$[37] |
| Surface modifiers | Y[25] Nb[26] $LiFeO_2$[27] | |
| Fabrication techniques | Hot pressing, sintering & slurry casting | Hot pressing, hot rolling, plasma spraying & tape casting |

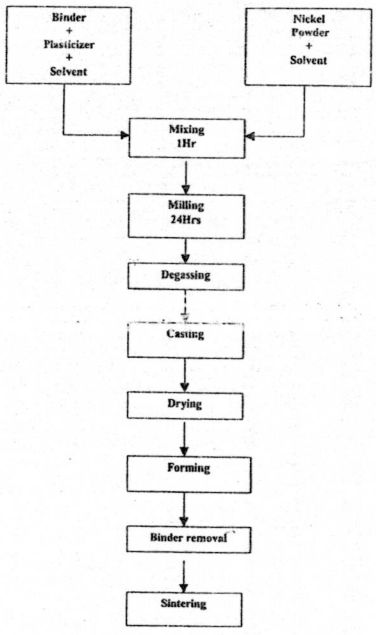


*Fig. 2: Fabricatiion process for nickel electrodes for MCFC by aqueous tape casting*

with the literature values [32]. The density values reported by us are the tap density values while the values reported in literature are loose powder or bulk (apparent) density values. It is reported in literature that the lower bulk density values of types 255 and 287 Ni powders result in sintered plates with higher porosities [33], making them as suitable candidates for battery applications.

The density values of the hydrogen treated powders are higher than the untreated powders indicating that the particles are in close contact after hydrogen treatment. The use of hydrogen treated nickel powders may result in lower porosity values for the sintered plates than when untreated powders were employed.

The characteristics of the nickel electrodes prepared by loose powder sintering method are indicated in Table III. The density values of the sintered plates are close to the closely packed powder density values. The sinter density values of treated powder packs are higher than the untreated powder packs. The porosity values obtained are lower than the porosity values reported in [32]. This is probably due to the difference in sintering conditions employed by us. Higher sintering temperatures result in lower porosity values. Increase of sintering time beyond 30 - 60 minutes may not have much influence on porosity. But both of them were reported to influence the strength of the sintered body [33]. Improved strength and conductivity accompany a decrease in porosity as a consequence of the increase in bond area formed between particles. These sintering conditions become vital in achieving optimum electrode porosity.

The porosity of the compacts made from type 123 powder was found to be less than those obtained from type 255 or 287 powders. Though the experimental values are lower than the literature values, the trend remains the same. It is reported that the more spherically shaped type 123 powder with a high bulk density results in a denser sintered plaque, with a smaller pore dia. This seems that this powder is more suitable for the anode plaque requirements of MCFC. While the relatively higher porosity values obtained with type 255 and 287 powders suggest that the sintered plaques formed from them will be suitable for the cathode specifications. Mixing of the two powders can further be utilized to control the pore microstructures within the desired range. Efforts are on in this direction.

Unlike the anode, the cathode requires electrodes with higher porosity and broader pore spectrum. Slurry casting method has been developed and reported using aqueous poly vinyl alcohol or methyl cellulose as binders [34,35]. A similar process has been adopted by us. The sintering conditions are determined by the TGA and DTA analysis of the green nickel tapes. A typical DTA/TGA curve of the green nickel tape is shown in Fig. 3. Initially, there is a steady weight loss upto 383 K indicating that water from the green tape is removed. On further heating, a secondary weight loss is noticed upto 643 K indicating the plasticizer and binder materials are removed. Nickel starts oxidising at temperature

**TABLE II: Comparison of the INCO Ni powder types**

| | INCO 255 | INCO 287 | INCO 123 |
|---|---|---|---|
| Average particle size (μm) | 2-3 | 2.6-3.3 | 3-7 |
| Bulk density (g/cc)@ | 0.5-0.65 | 0.75-0.95 | 1.8-2.7 |
| **Tap density values**** | | | |
| Before heat treatment | 1.581 | 1.506 | 3.486 |
| After $H_2$ treatment | 2.015 | 1.624 | 3.557 |

@ Reported reference [29] ** Our experimental

**TABLE III: Characteristics of nickel electrodes prepared by loose powder sintering**

| Ni type | $Ni_{255}$ | | $Ni_{287}$ | | $Ni_{123}$ | |
|---|---|---|---|---|---|---|
| characteristics | UT | T | UT | T | UT | T |
| Density (sintd) (g/cc) | 1.661 | 2.876 | 1.463 | 1.848 | 3.435 | 3.525 |
| Porosity (%) | 62.340 | 64.110 | 79.230 | 68.180 | 48.180 | 46.900 |
| Theoretical value [28] | 90.000 | ---- | 86.000 | ---- | 60.000 | ---- |

UT - Ni powder untreated

T - Ni powder after hydrogen pretreatment

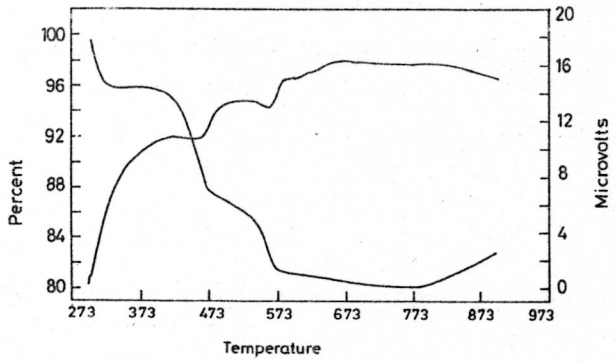


*Fig. 3: DTA/TGA curve of the Ni tape*

above 673 K in air. This is useful in determining the temperature profile during the sintering stage.

Consequently the electrodes are sintered in $H_2$ atmosphere at a slow heating rate of 1 K/min, with intermittent soaking stages at 423 K for 3 h and 673 K for 3 h to remove the inorganic and organic constituents. The final sintering temperature is 1073 K for one hour and the product is cooled to room temperature at 1 K/min.

Table IV indicates the characteristics of green tapes and the sintered electrodes prepared from these tapes after controlled sintering. Both the shrinkage factor, density values of the green and sintered plaques and the final porosity values are reported. The density of the green compact depends upon the binder content (wt%), slurry composition, solvent(water) content, plasticizer amount and casting rates [35]. In this case also, both the green and sinter density values for the Ni electrodes from Ni-123 powder are higher than the tapes employing Ni-255 or Ni- 287 powders. The porosity values from Ni-287 tapes are higher than tapes from Ni-123 powder making them more suitable as cathodes.

A number of methods have been reported to prepare lithiated nickel oxide cathodes [36-39]. The most widely adopted method is the in-cell lithiation technique, where a sintered Ni plaque is used as the cathode. At the operating temperature of the fuel cell i.e., at 923 K, the nickel is oxidised to NiO under incell conditions and the $Li_2CO_3$ from the electrolyte reacts with the NiO making it lithiated. Prelithiated nickel oxide powders were also used to prepare the electrodes by either loose powder sintering or tape casting methods. But these methods were found to result in lower porosity values. But the tapes prepared from

**TABLE IV: Characteristics of nickel electrodes prepared by tape casting method**

| Ni type | $Ni_{123}$ | | $Ni_{255}$ | | $Ni_{287}$ | |
|---|---|---|---|---|---|---|
| characteristics | UT | T | UT | T | UT | T |
| Thickness (mm) (green) | 0.768 | 0.706 | 1.156 | 1.050 | 1.220 | 1.072 |
| Thickness (mm) (sintd) | 0.725 | 0.513 | 0.868 | 0.835 | 0.873 | 0.856 |
| Shrinkage (%) | 5.6 | 27.3 | 24.9 | 20.3 | 28.4 | 20.1 |
| Density (g/cc) (green) | 3.110 | 3.170 | 1.705 | 2.233 | 1.428 | 2.000 |
| Density (g/cc) (sintd) | 3.167 | 3.276 | 2.714 | 3.124 | 1.750 | 3.236 |
| Porosity (%) | 40.420 | 35.620 | 57.660 | 52.110 | 65.990 | 64.290 |

UT - Ni powder untreated
T - Ni powder after hydrogen pretreatment

prelithiated powder were used in the cell as green tapes and the electrodes were sintered under insitu condition. This had resulted in better performance of the cells than while employing presintered cathodes. The details of this process, conditions employed and advantages will be reported shortly.

## CONCLUSION

The characteristics of the nickel electrodes prepared from three types of commercial Ni powders were compared. The sintered electrode from type 287 and 255 offer as choice for the cathodes and type 123 powder or mixtures can be employed for the anode. Tape casting is a convenient method of making porous nickel electrodes.

***Acknowledgement:*** The authors express their thanks to Dr V Sundaram for his help in the DTA/TGA results. The financial assistance from MNES, New Delhi is gratefully acknowledged.

## REFERENCES

1. K Kinoshita, F R Mc Larnon and E J Cairns *"Fuel Cells - A Hand Book" DOE/METC* - **88/6096** (1988) Chapter 4
2. S S Penner, *Assessment of Research Needs for Advanced Fuel Cells,* (US Dept of Energy, Washington DC) (1985) DOE Report DE- AC0184ER30060 T1
3. C D Iacovangelo, *J Electrochem Soc,* **133** (1984) 2410
4. H Yabe, Y Ito, K Ema and J Oishi, *J Power Sources,* **24** (1988) 207
5. T Hashino and T Kohno, *Proc the International Fuel Cell Conference,* Makahuri, Japan Feb 3-6, (1992), III-B-4, 169
6. A Pigeaurd, H C Maru, L Paetsch, J Doyon and R Bernard, *in Proc Symp Porous Electrodes, Theory and Practice,* Eds

H C Maru, T Katan and M G Klien, *The Electrochem Soc,* Pennington, NJ (1984) 234
7. C E Baumgartner, R H Arendt, C D Iacovangelo and B R Karas, *J Electrochem Soc,* **131** (1984) 2217
8. EPRI Proc DOE/EPRI Workshop on MCFC (EPRI Palo Acto CA (1979) Report No WS-78-135
9. Development of Improved Molten Carbonate Fuel Cell Technology, *Final Report on EPRI contract No RP-1085-4* (UTC) July (1983)
10. C D Iacovangelo, *J Electrochem Soc,* 133 (1986) 280
11. O Lanzi and V Landaun, *J Electrochem Soc*, **137** (1990) 585
12. C E Baumgartner, *J Amer Cera n Soc,* **73** (1990) 516
13. L Blomen and M Mugerwa (Eds), *Fuel Cell Systems,* Plenum Press New York (1993)
14. L G Marianowski, R A Donado and H C Maru, *U S Pat 4,247,604* (1981)
15. M Tachuchi, *Programm and Abstracts* (1988) Fuel Cell Seminar, Long Buch, California, (1988)
16. L Paetsch, J Doyon, R Chemberlin and C Yuh, *Extended Abstracts of Electrochem Soc*, meeting 87-2, Pennigton, New Jersey (1987)
17. D S Erickson, E T Ong and R Donedo, *Programm and Abstracts of 1986,* Fuel Cell Seminar Tucson, Arizona (1986)
18. H H Angerman, F K Yang and O Van der Biest, *Intl J Powder Metallurgy,* **28** (1992) 361
19. S Yamenaka, G Maruyama and T Ueyama, *J Ceram Soc Japan,* **110** (1992) 657
20. L Suski and J Wyrwa, *J Appl Electrochem,* **20** (1990) 625
21. J Seo, S Kuk and K Kim, *J Kor Chem Soc,* **40** (1996) 180
22. E R Hwang, J W Park, Y D Kim, S J Kim and S G Kang, *J Power Sources,* **69** (1997) 55
23. P Singh and M Benedict, *U S Pat,* **4, 659, 379** (1987)
24. I H Oh, S P Yoon, T H Lim, S W Nam, S A Hong and H C Lim, *Denki Kagaku* **64** (1996) 497
25. G Xie, K Enaa and Y Ito, *J Appl Electrochem,* **24** (1994) 368
26. P Taxil and J Maheng, *J Appl Electrochem,* **17** (1987) 457
27. S H Lu, *J Electrochem Soc,* **142** (1995) 3812
28. T Trechtenberg, *J Electrochem Soc,* **111** (1964) 110
29. M Franka and Jack Winnick, *J Electrochem Soc,* **135** (1988) 1595
30. S Dheenadayalan, C Solaiyan, P Gopalakrishnan, R Chandrasekaran and R Pattabiraman, *Powder Metallurgy Newsletter,* **14** (1988) 70
31. S Dheenadayalan, C Solaiyan, I Arul Raj, S Muzhumathi, R Chandrasekaran and R Pattabiraman, *Submitted to Ind J Technol,* (1998)
32. V A Traccy and R P Perks, *Powder Metallurgy*, **12** (1963)
33. V A Traccy and N J Williams, *Electrochem Technol*, **3** (1965) 1
34. A Pigeaurd, Report No CHI/11304-19 for DOE Energy Research Corporation Danbury, CT, (1980)
35. M Watanabe, M Takao and Y Namikawa, *Denki Kagaku*, **57** (1989) 898
36. N Q Minh, *J Power Sources*, **24** (1988) 1
37. J R Selman and T D Claar *in "Proc Symp Molten Carbonate Fuel Cell Technology,"* Ed by J R Selmann and T D Claar Pv 84-13, *The Electrochemical Society Inc,* Pennington, NJ, USA (1984) pp 108-112
38. E Antolini, *J Power Sources*, **40** (1992) 265
39. C Baumgartner and K P Zarnoch, *Amer Ceram Soc Bull*, **64** (1985) 593